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^1H and ^{13}C solution- and solid-state NMR investigation into wax products from the Fischer-Tropsch process

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Abstract

^1H and ^{13}C solid- and solution-state NMR have been used to characterise waxes produced in the Fischer-Tropsch reaction, using Co-based catalysts either unpromoted or promoted with approximately 1 wt% of either cerium or rhenium. The aim was to measure average structural information at the submolecular level of the hydrocarbon waxes produced, along with identification of the minor products, such as oxygenates and olefins, which are typically observed in these waxes. A parameter of key interest is the average number of carbon atoms within the hydrocarbon chain (N_{C}). A wax prepared using an unpromoted Co/Al₂O₃ catalyst had $N_{\text{C}} \sim 20$, whilst waxes made using rhenium- or cerium-promoted Co/Al₂O₃ catalysts were found to both have $N_{\text{C}} \sim 21$. All three samples contained small amounts of oxygenates and alkenes. The subtle differences found in the waxes, in particular the minor species produced, demonstrate that the different promoters have different effects during the reaction, with the Re-promoted catalyst producing the fewest by-products. From a technique point of view it is shown that the longer chain (compared to the lengths of chain in previous studies) waxes that the lack of resolution and the complexities added by the differential cross-polarisation (CP) dynamics mean that it is difficult to accurately determine N_{C} from this approach. However the N_{C} determined by ^{13}C CP magic angle spinning NMR is broadly consistent with the more accurate solution approaches used and suggest that the wax characteristics do not change in solution. On this basis an alternative approach for determining N_{C} is suggested based on ^1H solution state NMR that provides a higher degree of accuracy of the chain length as well as information on the minor constituents.

Introduction

In the early 1900s it was discovered that the formation of hydrocarbons from the reaction of H_2 and CO at high temperatures (200°C) and pressures (20 bar) was possible in a process known as the Fischer-Tropsch (FT) reaction.¹⁻⁴ Although the exact mechanism of the reaction is still the subject of debate,⁵⁻⁶ the reaction converts synthesis gas (a mixture of hydrogen and carbon monoxide) into long chain paraffins, with chain lengths of 100 or more carbons in some cases. These waxes are further processed to the diesel hydrocarbon fraction ($n \sim 12\text{-}22$). The FT process is therefore a key part of processes to convert non-oil feedstocks such as gas, coal or biomass into liquid transportation fuels. The catalysts of interest in the current work are cobalt-based, supported on alumina; either cobalt-only or containing approximately 1% of a promoter, rhenium (Re),⁷⁻¹⁰ or cerium (Ce).¹¹ Promoters are added to the catalyst to improve performance in different ways.

Three waxes produced using the above catalysts are analysed here. The waxes are characterised using both solid- and solution-state NMR in order to measure the average number of carbon atoms within the hydrocarbon chain (N_C), as well as characterising subtle differences in the by-products, such as oxygenates and alkenes. The FT process is known to produce small amounts of these by-products,¹² and the amount produced depends on the choice of catalyst and reaction conditions. It is hoped that information on the products generated by the different catalysts will give a greater understanding of the catalysts used.

Little structural information on the by-products in these waxes is available and hence the aim of this work is to use both solution- and solid-state NMR to characterise them. The waxes contain a complex mixture of molecules, although it is expected that they are predominantly saturated hydrocarbons in linear form. Due to

the complication with various forms of carbon chains, the identification of every compound present is not feasible. For this reason NMR spectroscopy is of great use, in particular with the goal of deducing average structural information at the submolecular level on the wax materials. The waxes produced are usually characterised by gas chromatography, which separates each component. NMR analysis offers the opportunity to analyse the whole sample and so has significantly better sensitivity for non-hydrocarbon functionalities present in low levels.

NMR of hydrocarbons has been used to characterise many different compounds in both solution-state¹³⁻¹⁶ and solid-state NMR.¹⁷⁻²⁰ However, because of the low natural abundance of ^{13}C , 1.1%, the Cross-Polarisation (CP) experiment²¹⁻²³ is used to enhance the signal sensitivity for ^{13}C . For solid-state NMR, CP is often combined with Magic Angle Spinning (MAS).²⁴⁻²⁵ The ^{13}C and ^1H isotropic chemical shifts have been well documented for long chain hydrocarbons in the solution state,²⁶⁻²⁸ however, only ^{13}C data has so far been reported in the solid state.²⁹⁻³² To gain further information on the product waxes in solution a combination is used of one-dimensional experiments along with both Polarisation Enhancement During Attached Nucleus Testing (PENDANT)³³⁻³⁴ and Heteronuclear Multiple-Quantum Coherence (HMQC)³⁵⁻³⁶ approaches.

Although solid-state ^{13}C NMR was first used to characterise hydrocarbons in the late 1970s³⁷⁻³⁸ it was not until 1985 that Cookson and Smith quantified N_{C} in hydrocarbon fuels using ^{13}C NMR spectroscopy.³⁹ The fractional abundances of CH_n groups were measured ($n = 0$ to 3) by using a gated spin-echo (GASPE) technique. The GASPE technique gives subspectra for each of the CH_n groups for ease of calculating fractions of each group. However, due to the advances in high-field NMR spectrometers, it is now possible to measure high-resolution ^{13}C CP-MAS spectra

with some resolution of the different CH_n . Hence, the complicated GASPE approach is not necessary in the current work.

For a linear alkane such as in Figure 1, the empirical formulae takes the form of C_nH_{2n+2} . Assuming no branching, Cookson and Smith found one resonance corresponds to the terminal αCH_3 groups, and four (β , γ , δ and ϵ) to the CH_2 groups. Moreover, it was also found that any CH_2 groups beyond ϵCH_2 have negligible effect on the chemical shift of the CH_3 terminations. The observed five resonances are found in the ^{13}C NMR spectra to be at 14.3 ppm (αCH_3), 23.0 ppm (βCH_2), 32.2 ppm (γCH_2), 29.7 ppm (δCH_2) and 30.0 ppm (ϵCH_2) for a hydrocarbon chain of $(\alpha\text{CH}_3)_2(\beta\text{CH}_2)_2(\gamma\text{CH}_2)_2(\delta\text{CH}_2)_2(\epsilon\text{CH}_2)_y$.³⁹

The average n-alkane chain length, N_C , can be calculated from Cookson's Formula.³⁹

$$N_C = \frac{8I(\alpha, \beta, \gamma, \delta, \epsilon)}{I(\alpha, \beta, \gamma, \delta)} \quad (1)$$

where I is the total ^{13}C NMR intensity of different carbon groups listed in parenthesis. With modern NMR instruments, in some cases the different carbon groups can be resolved allowing each resonance to be integrated separately. Thus, the Cookson formula can be rewritten as,

$$N_C = \frac{8I(\text{all } \text{CH}_n \text{ groups})}{I(\text{all } \text{CH}_n \text{ groups}) - I(\epsilon\text{CH}_2 \text{ group})} \quad (2)$$

where $n = 2$ or 3 . The Cookson formula has also been used to calculate N_C for alkenes and alkanes synthesised from Fischer-Tropsch products⁴⁰ and waxes similar to those studied in the current work.⁴¹

In solution-state, N_C is determined from ^1H NMR as ^{13}C NMR is potentially non-quantitative due differential effects of 1H decoupling. The integrated intensity of the terminal CH_3 peak in the solution-state ^1H NMR spectrum is used to normalise the

number of protons responsible for each peak. A similar analytical method is used to calculate the cetane number of diesel fuels.⁴²

Experimental Details

Materials

Before any Fischer-Tropsch waxes were examined, some standards were measured. The standards used were Docosane ($C_{22}H_{46}$) (99%, Alfa-Aesar) and Octacosane ($C_{28}H_{58}$) (99%, Alfa-Aesar). The three Fischer-Tropsch waxes have been collected over the entire duration of a 120 hour FT reaction using Co-only, or Re- or Ce-promoted Co/ Al_2O_3 catalysts. The measured N_C of these waxes reflect the nature of the collection process as much as any property of the catalyst performance or test method. The waxes are referred to as “Co-wax”. “ReCo-wax” and “CeCo-wax” throughout this paper.

NMR experimental details

Standard 1D 1H and ^{13}C solution-state NMR spectra were taken of the waxes using a 270 MHz BSX 270 Jeol spectrometer (6.35 T). The 1H NMR spectra were acquired using a single pulse with a pulse delay of 2 s and 16 acquisitions. ^{13}C NMR spectra were acquired with a pulse delay of 0.25 s and 25000 acquisitions. Deuterated chloroform, $CDCl_3$, was used as a solvent for all waxes and the ^{13}C chemical shift reference. The waxes showed good solubility in $CDCl_3$ and there was no evidence of insoluble residues.

To gain further information on the by-products in selected waxes, a 500 MHz Bruker spectrometer (11.7 T) was used to perform solution-state ^{13}C PENDANT and 2D HMQC NMR correlation experiments between ^{13}C and 1H . Samples were held in a 5 mm BBO probe. The ^{13}C PENDANT experiments were taken with 128

acquisitions, a 90° pulse length of 6.6 μs and a pulse delay of 2 s. The 2D HMQC correlation experiments were taken with 40 acquisitions at each ^1H position, a 90° pulse length of 8.8 μs and a pulse delay of 1.8 s.

Standard 1D solid-state ^{13}C CP/MAS NMR spectra were taken of the waxes using either a Varian InfinityPlus 300 MHz (7.05 T) or Bruker Avance II⁺ 600 MHz (14.1 T) spectrometer. Samples were held in a 4 mm Bruker MAS rotor and spun at 10 kHz or 15 kHz. A CP pulse sequence was used with a 90° pulse length of 2.5 μs , pulse delay of 3 s, the contact time between ^1H and ^{13}C spins was set to either 1 ms or 4 ms. 20000 transients were acquired over 17 hours. ^1H MAS NMR was performed on a Bruker Avance II⁺ 600 MHz spectrometer under identical sample conditions as for the ^{13}C MAS NMR described above. The ^1H 90° pulse length was 2.75 μs and 972 transients were acquired.

Results and discussion

^{13}C NMR Spectra

Solid state ^{13}C NMR spectra were obtained for docosane (Figs 2, 3), as well as solution spectra, including that of octacosane (Fig. 4). Similar combinations of solid and solution state ^{13}C NMR data is shown from the three wax samples – Co-wax (Fig. 5), ReCo-wax, Fig. 6(a) and CeCo-wax, Fig. 6(b). The spectra were fitted using DMFit⁴³. All four spectra show peaks for the α -carbon at 14-16 ppm, the β -carbon at 24-26 ppm and the other carbon atoms (γ , δ and ϵ) in a complex peak or group of peaks at 28-38 ppm. These are in broad agreement with the results of Cookson and Smith³⁹ for their shorter-chain alkanes in solution-state ^{13}C NMR. However, the chemical shifts observed in this work are slightly higher than those analysed by Cookson and Smith by 2-5 ppm. This is likely to be a consequence of (1) a longer carbon chain length and (2) the packing of the alkane chains in the solid wax, giving an extra intermolecular van der Waals force which is not observed in the solution state. An additional peak is observed at 53 ppm in the spectrum of ReCo-wax. This is assigned as an oxygenated species, such as C-OH .

Attempts were made to determine N_{C} using the Cookson formula, but these were hampered by the poor resolution of the γ - and δ -carbon peaks from the ϵ -carbon peak. The ϵ -carbon peak is much larger in these longer chain wax samples than the kerosene and diesel peaks analysed by Cookson and Smith. The other difficulty in determining N_{C} from ^{13}C MAS NMR data is the effect of contact time on the spectrum. Spectra were measured at 1 and 4 ms contact times for ReCo-wax and CeCo-wax, and a modified Cookson formula applied normalised to the four α - and β -carbons in the sample:

$$N_C = \frac{4I(\text{all } CH_n \text{ groups})}{I(\alpha CH_3 \text{ groups}) + I(\beta CH_2 \text{ group})} \quad (4)$$

The N_C values calculated using this approach were not consistent at the two contact times, and this was initially thought to be due to a different enhancement of the α -carbon, which has three protons attached to it. A second modification of the Cookson formula normalised on the β -carbon only was applied:

$$N_C = \frac{2I(\text{all } CH_n \text{ groups})}{I(\beta CH_2 \text{ group})} \quad (5)$$

However, this did not yield improved values and so the method was deemed unreliable. This is due to (1) poor resolution of the γ -, δ - and ϵ -carbon peaks and (2) the non-linear enhancement of the signal with CP contact time. Interestingly, the standard docosane does not change as much as the FT waxes with contact time. This could suggest a role of minor impurities or variable chain length as the cause of the difficulties in determining N_C .

The samples were also analysed by solution state NMR, dissolved in deuteriochloroform (Figs 4-6). All the samples showed good solubility in the solvent at room temperature. The same chemical shifts were observed for all the samples: 14, 23, 32, 29.5 and 30 ppm for the α -, β -, γ -, δ - and ϵ -carbons respectively. These were slightly lower than the values obtained by ^{13}C MAS NMR above, and in good agreement with the data of Cookson and Smith³⁹. N_C calculations were not attempted using this data as the spectra were obtained in proton-decoupled mode and therefore are not quantitative.

A smaller peak was observed in the spectrum of the ReCo-wax and CeCo-wax samples at 64 ppm (although not the Co-wax or the standard materials). As it is a weak signal in both cases, the samples were investigated by solution-state ^{13}C PENDANT NMR (Fig. 7). The PENDANT spectra confirm the assignments of the

major peaks (the α -carbon is negatively phased as a CH_3 group, whilst the others are positively phased as CH_2 groups). The PENDANT spectra also show a number of small peaks in both samples – positively-phased peaks at 61 and 74 ppm, and negatively phased peaks in the 120-140 ppm region. The former are in the region usually assigned to carbon-carbon triple bonds (alkynes), oxygenates or quaternary carbons. The positive phasing means that a C-OH functionality is ruled out as the carbon will only have one hydrogen attached. However, an ether-type linkage ($-\text{CH}_2-\text{O}-\text{CH}_2-$) would be consistent with the data. There are multiple peaks in the 120-140 ppm range, and they are less intense than the peaks at 64 and 71 ppm. These are assigned to alkene functionalities, with the exact position of the peak depending on its position in the chain. The PENDANT NMR shows that these alkenes are predominantly internal alkenes ($-\text{CH}=\text{CH}-$) rather than terminal alkenes ($\text{H}_2\text{C}=\text{CH}-$) as all the peaks are negatively phased. Cobalt catalysts in the FT process do not make aromatics⁴⁴ (they are only produced using iron catalysts, and even then are thought to be secondary products⁴⁵) and so these are unlikely to be due to benzene ring species.

^1H NMR Spectra

To investigate the application of solid-state ^1H NMR to the analysis of the waxes, the ReCo-wax and CeCo-wax samples were analysed (Fig. 8). These showed the expected resonances for methyl (0.7 ppm) and methylene (1.0 ppm) protons. The latter was a poorly-resolved peak. In addition, in both spectra an additional peak was observed at 4.1 ppm. This is assigned to oxygenate groups, such as $\text{CH}-\text{OH}$ or CH_2-O . The chemical shifts observed in the solid state proton spectra for methyl and methylene protons are both slightly lower than those in the solution state spectra (see below). This may be a consequence of packing effects in the solid state.

As for the solution state ^{13}C spectra above, solution-state ^1H data were obtained in deuteriochloroform solution. The solution-state ^1H NMR spectra of the standards (docosane and octacosane) and Co-wax (Fig. 9), alongwith ReCo-wax and CeCo-wax (Fig. 10) were all recorded. The peaks for methylene and methyl protons were located at 1.2-1.25 and 0.85-0.95 ppm respectively, in line with previous work⁴². The average carbon chain length was calculated by careful integration of these peaks, using a modification of the Cookson approach³⁹:

$$N_{\beta} = \frac{1}{2} \times \frac{6I_{\beta}}{I_{\alpha}} \quad (6)$$

where N_{β} is the number of CH_2 carbons, I_{β} is the total intensity of the methylene protons and I_{α} is the intensity of the six methyl protons. The total chain length is then found by adding two methyl carbons to the number of methylene carbons:

$$N_c = \frac{3I_{\beta}}{I_{\alpha}} + 2 \quad (7)$$

This assumes that there is no branching in the wax – i.e. that there are only two methyl groups per chain. This is a reasonable assumption for FT waxes as the mechanism strongly favours straight chain alkane over branched chain alkane formation⁴⁶. The results calculated using equation 7 are shown in Table 1. The results for the two standards, docosane and octacosane, were in excellent agreement with the expected values. The three wax samples were all close in average chain length, being 20-22 carbons long. This may be a reflection of the sampling method as much as of the different catalysts used to make the wax.

Additional peaks were observed in the wax samples using ^1H NMR. Some of these are trivial to account for – tetramethylsilane at 0 ppm, water around 1.6-2.0 ppm and acetone from tube cleaning at 2.15 ppm. The other peaks are more interesting and assigned to impurities in the waxes. No impurities were observed in the two

standards, which is not surprising as they were purchased as high-purity materials from commercial suppliers. In contrast, the FT wax samples contained small peaks which fell into two groups – 3.2-4.2 ppm, assigned to oxygenated species, and 4.5-5.5 ppm, assigned to alkenes. It is interesting to note that the peaks were different for the three FT wax samples. The amount of these impurities was calculated using the following formula

$$H_{imp}(\%) = \frac{100 \times I_{imp}}{I_{tot}} \quad (8)$$

where H_{imp} is the percentage of the protons in the sample which are present in the impurity, I_{imp} is the integrated intensity of the impurity, and I_{tot} is the intensity of all the protons in the sample. The relationship to the number of functional groups of a different type will depend on the nature of the group.

The values calculated using equation 8 are tabulated in Table 2, which show them all to be minor phases compared with the alkane methylene and methyl protons. This is expected as a consequence of the mechanism of the FT reaction, which is very selective for straight chain alkanes, especially when cobalt catalysts are used⁴⁶.

In order to further understand the nature of the impurities, 2D HMQC analyses were performed on the ReCo-wax and CeCo-wax samples. This solution-state technique allows the ^1H and ^{13}C NMR spectra to be correlated, allowing extra information to be derived from the experiments. Figure 11(a) shows the 2D HMQC spectrum of the ReCo-wax sample. The main peaks for methyl and methylene groups are strongly correlated, as expected.

More interesting are the impurity peaks. The peaks at 3.3 and 3.7 ppm in the ^1H spectrum are strongly correlated with the ^{13}C peaks at 80 and 63 ppm respectively. This suggests two different oxygenate environments are present. No carbonyl carbons

were observed by ^{13}C NMR, either in the solid state or in solution, so a group such as $-\text{CH}_2-\text{C}=\text{O}$ is not likely to be present. The chemical shift value suggests that the protons are directly attached to the carbon containing the oxygenate, and therefore the two resonances are tentatively assigned to $-\text{CH}(\text{OH})-$ and $-\text{CH}_2-\text{O}-\text{CH}_2-$ at 3.7 and 3.3 ppm respectively. The ^{13}C chemical shift of $-\text{CH}(\text{OH})-$ will be lower than that of $-\text{CH}_2-\text{O}-\text{CH}_2-$ as its carbon is bonded to two other carbons and one hydrogen, compared with two hydrogens and one carbon. Oxygenate groups are thought to arise in FT products as a consequence of the incorporation of undissociated CO molecules or by hydrolysis of alkene functionalities⁴⁷, and both these groups would be in agreement with this hypothesis.

The peaks at 5.0 and 5.4 ppm in the ^1H spectrum are correlated to peaks in the ^{13}C spectrum at 160 and 130 ppm respectively, and are assigned to alkene groups. It seems likely that the 5.0 ppm peak relates to an α -carbon CH_2 group and the larger peak relates to internal CH alkene groups. There is a third peak at 5.8 ppm which may also be alkene in origin, but is not correlated to any peaks in the ^{13}C NMR spectrum. This may mean that the ^{13}C spectrum is too weak for the resonance to be observed. The CeCo-wax was also analysed by the 2D HMQC technique (Fig. 11(b)) and similar peaks were found for methyl and methylene peaks as the ReCo-wax. There were also oxygenate peaks as observed in the ReCo-wax, and a large doublet at 4.7 ppm in the ^1H spectrum. This peak was not correlated to any signal in the ^{13}C spectrum, which suggests that it may be a hydroxyl peak from an alcohol group. The position of OH peaks in ^1H NMR is known to depend strongly on the environment and sample, but they tend to be broad and featureless as seen in Fig. 11(b).

Summary of results

Both the standards, Docosane and Octacosane, show straight chain hydrocarbons with no evidence of by-products such as oxygenates or alkenes. The waxes produced by the Fischer-Tropsch reaction show small amounts of oxygenates and alkenes, up to 0.5 % in the ReCo-wax, 2.0 % in the Co-wax and around 3.3 % in the CeCo-wax. The levels of minor products are tabulated in Table 2. N_C was calculated for each sample and the results are summarised in Table 1. It can be clearly observed that for the solution-state results both standards show good agreement with the known values.

Conclusions

It has been demonstrated that both solid-state and solution-state (^1H , ^{13}C) NMR spectroscopy provide data that can potentially be used for characterising hydrocarbon waxes produced by the FT reaction. In general, solution-state NMR gives better results; however solid-state NMR provides results that are broadly consistent with the corresponding solution-state NMR results. Similar values were calculated for N_C using both approaches, and this suggests that the carbon composition in the solution phase is consistent with that in the solid phase, although the effects of resolution and differential CP dynamics create relatively large uncertainty in the ^{13}C solid state NMR results. We have examined the method used previously to analyse hydrocarbon fuels³⁹ and applied a modified version of the formula. However, our new solution-state ^1H NMR method is preferred due to better signal-to-noise ratio and quicker acquisition.

The waxes have a N_C value around 20–21 by solution state ^1H NMR. The similar value of N_C observed may reflect the collection method used for the waxes.

However, addition of as little as 1wt % of different promoters (Re or Ce) affects the product distribution. The low level of minor products in the different product waxes were characterised by the high-resolution 2D heteronuclear correlation experiment, and were found to be oxygenates and alkenes.

In this study, the waxes were sampled across the course of a long reaction and the product sampled by melting point, so the N_C values obtained are not related to the performance of the catalyst so much as the sampling method. This may explain why the numbers obtained are in such a small range ($N_C = 20-21$). However, the differences in the minor products observed do give some indication that the promoters change the product distribution observed. We believe that the NMR methods presented here can be used to give a good understanding of product selectivity in the higher carbon-number products of the Fischer-Tropsch reaction.

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Figure captions

Figure 1. Labelling of CH_n groups.

Figure 2. Solid-state ¹³C CP MAS NMR spectra of the standard Docosane (C₂₂H₅₄) taken at a field of 7.05 T, with contact times of 1 and 4 ms.

Figure 3. An expansion, between 10–45 ppm, of the solid-state ¹³C CP/MAS NMR spectrum and fit of the standard Docosane, taken at 7.05 T with a contact time of 4 ms and MAS frequency of 15 kHz. The spectrum is shown in blue and overall fit is shown in red.

Figure 4. ¹³C solution-state NMR spectra of the standards Docosane (C₂₂H₄₆) and Octacosane (C₂₈H₅₈) taken at a field of 6.35 T.

Figure 5. ¹³C CP/MAS NMR spectrum of the Co-wax taken at a field of 14.1 T with contact time 1 ms and MAS frequency of 10 kHz, and ¹³C NMR solution-state spectrum of the Co-wax taken at a field of 6.35 T.

Figure 6. ¹³C CP MAS NMR spectra at a field of 7.05 T, with contact times of 1 and 4 ms, and solution-state NMR spectra at a field of 6.35 T for (a) ReCo-wax and (b) CeCo-wax.

Figure 7. Solution-state ¹³C PENDANT NMR spectra taken at 11.75 T of (a) ReCo-wax and (b) CeCo-wax.

Figure 8. ¹H MAS NMR spectrum obtained at 14.1 T with spinning at 30 kHz of (a) ReCo-wax and (b) CeCo-wax.

Figure 9. ¹H solution-state NMR spectra taken at a field of 6.35 T of (a) octacosane (C₂₈H₅₈), (b) docosane (C₂₂H₄₆) and the Co-wax.

Figure 10. Solution-state ¹H NMR spectra taken at a field of 11.75 T of (a) ReCo-wax and (b) CeCo-wax.

Figure 11. 2D HMQC correlation NMR spectra taken at a field of 11.75 T of (a) ReCo-wax and (b) CeCo-wax. The *x*-axis displays the ¹H spectra and the *y*-axis displays the ¹³C spectra.

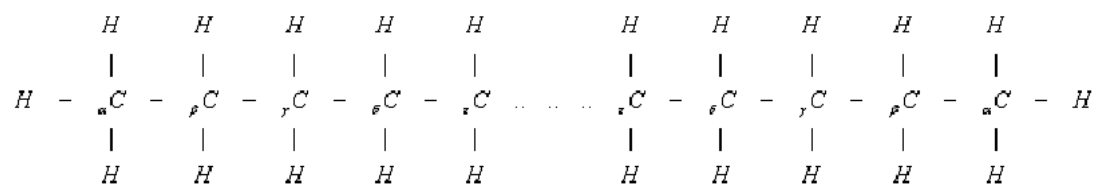


Figure 1. Labelling of CH_n groups.

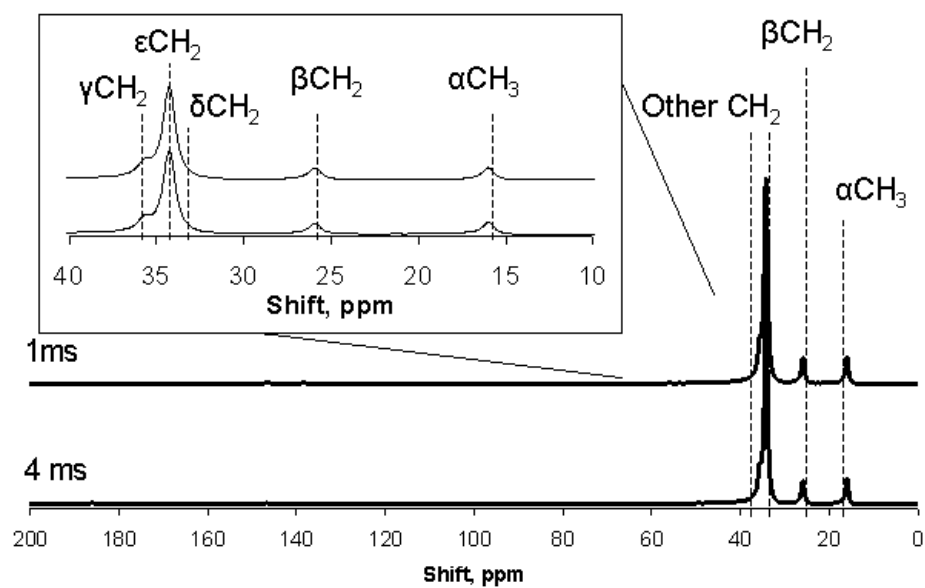


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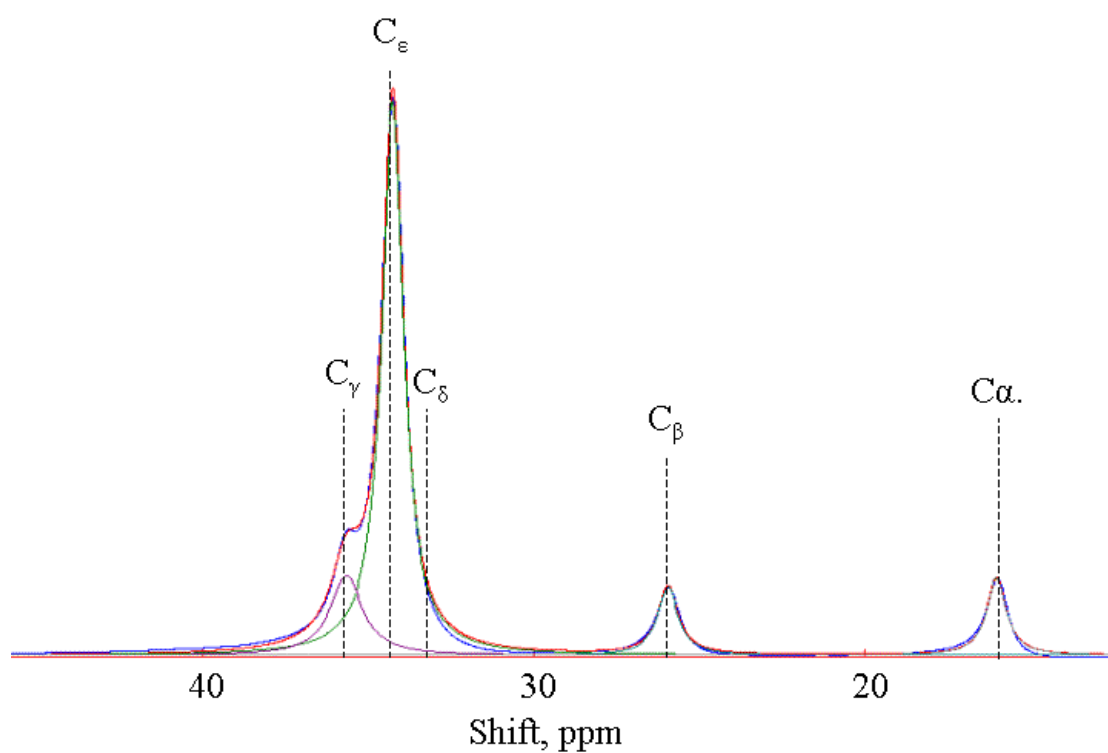


Figure 3. An expansion, between 10–45 ppm, of the solid-state ^{13}C CP/MAS NMR spectrum and fit of the standard Docosane, taken at 7.05 T with a contact time of 4 ms and MAS frequency of 15 kHz. The spectrum is shown in blue and overall fit is shown in red.

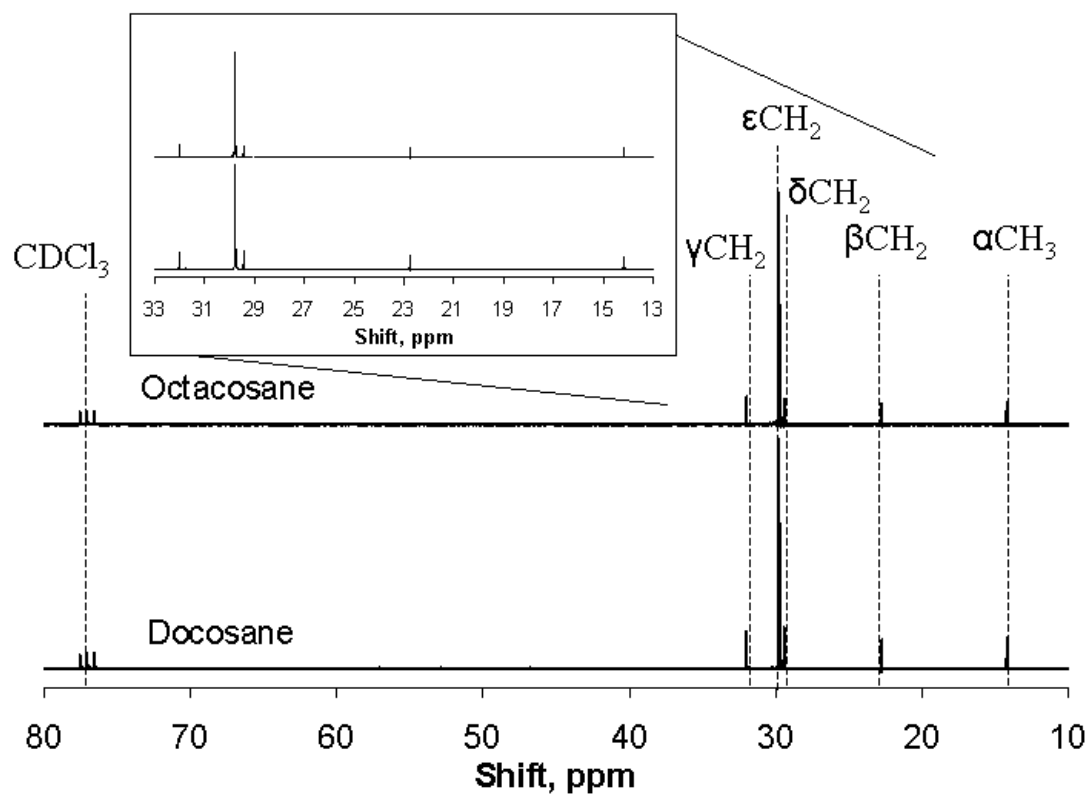


Figure 4. ^{13}C solution-state NMR spectra of the standards Docosane ($\text{C}_{22}\text{H}_{46}$) and Octacosane ($\text{C}_{28}\text{H}_{58}$) taken at a field of 6.35 T.

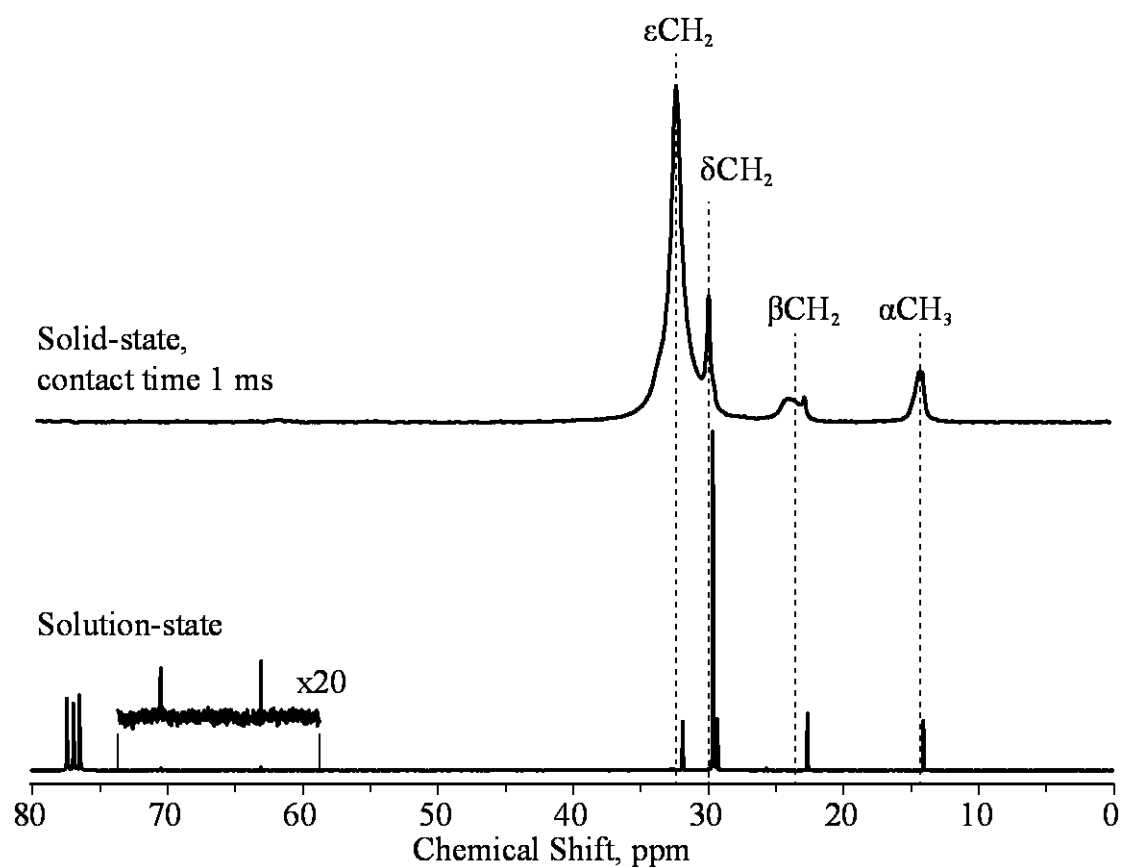


Figure 5. ^{13}C CP/MAS NMR spectrum of the Co-wax taken at a field of 14.1 T with contact time 1 ms and MAS frequency of 10 kHz, and ^{13}C NMR solution-state spectrum of the Co-wax taken at a field of 6.35T.

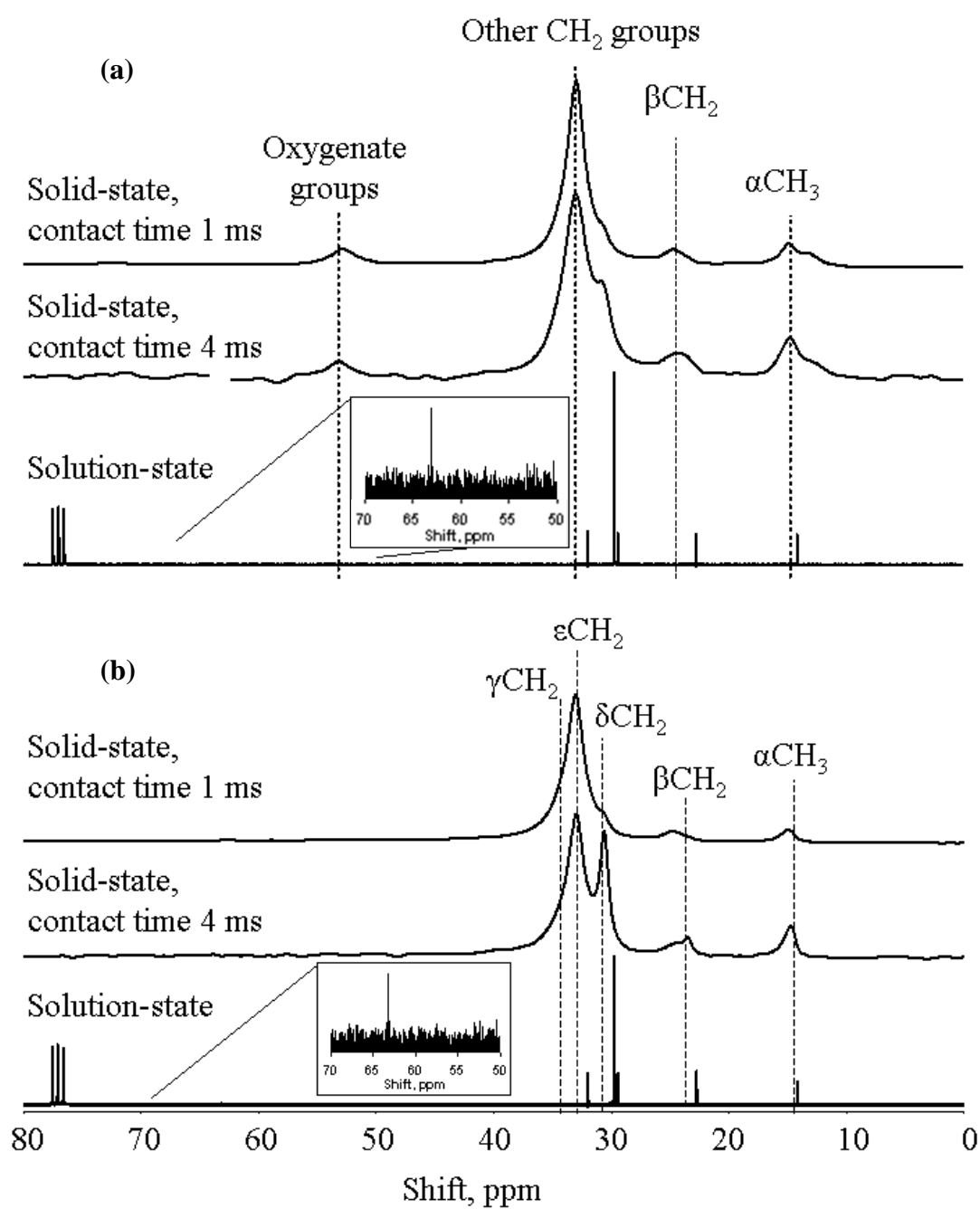


Figure 6. ^{13}C CP MAS NMR spectra at a field of 7.05 T, with contact times of 1 and 4 ms, and solution-state NMR spectra at a field of 6.35 T for (a) ReCo-wax and (b) CeCo-wax.

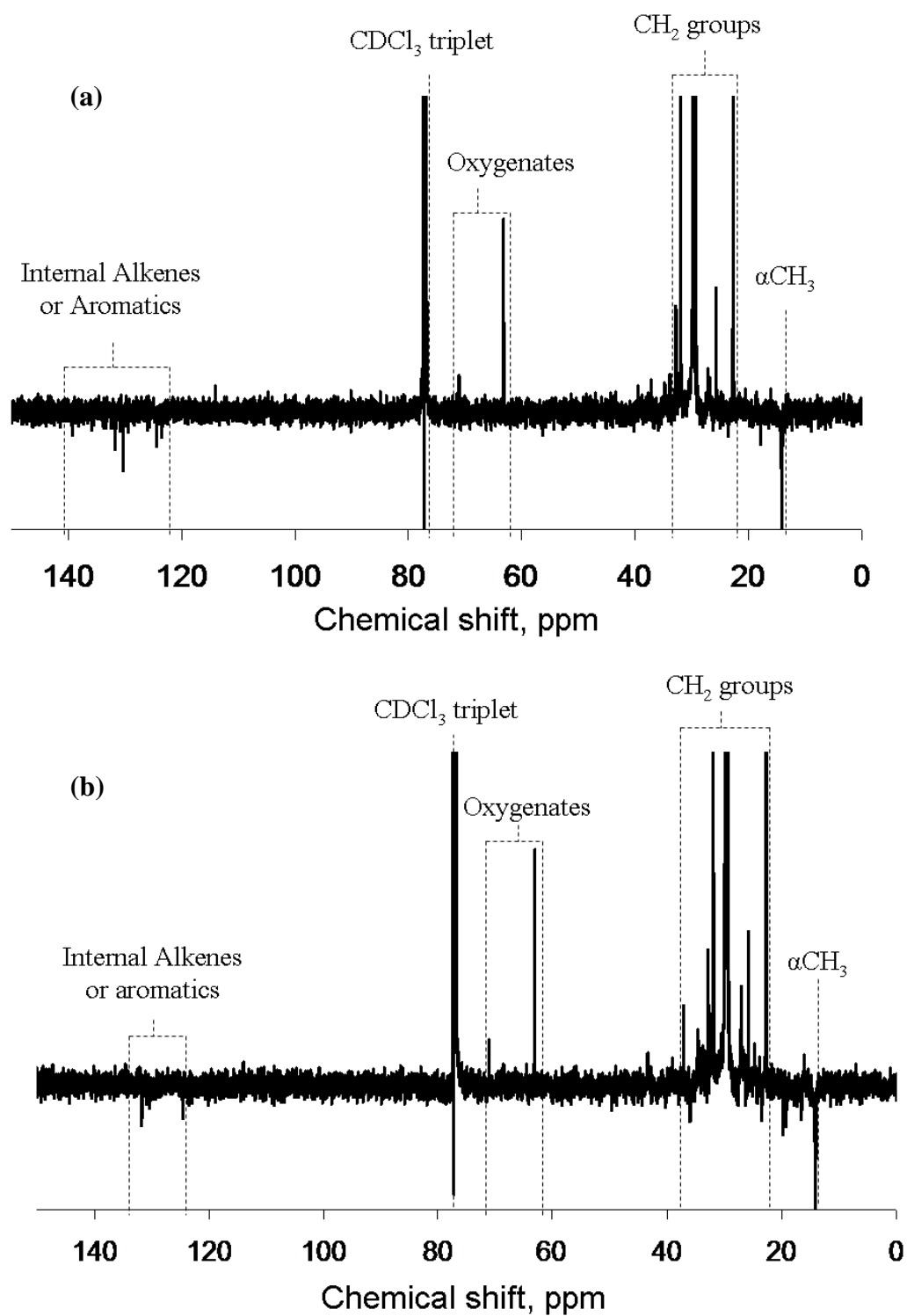


Figure 7. Solution-state ^{13}C PENDANT NMR spectra taken at 11.75 T of (a) ReCo-wax and (b) CeCo-wax.

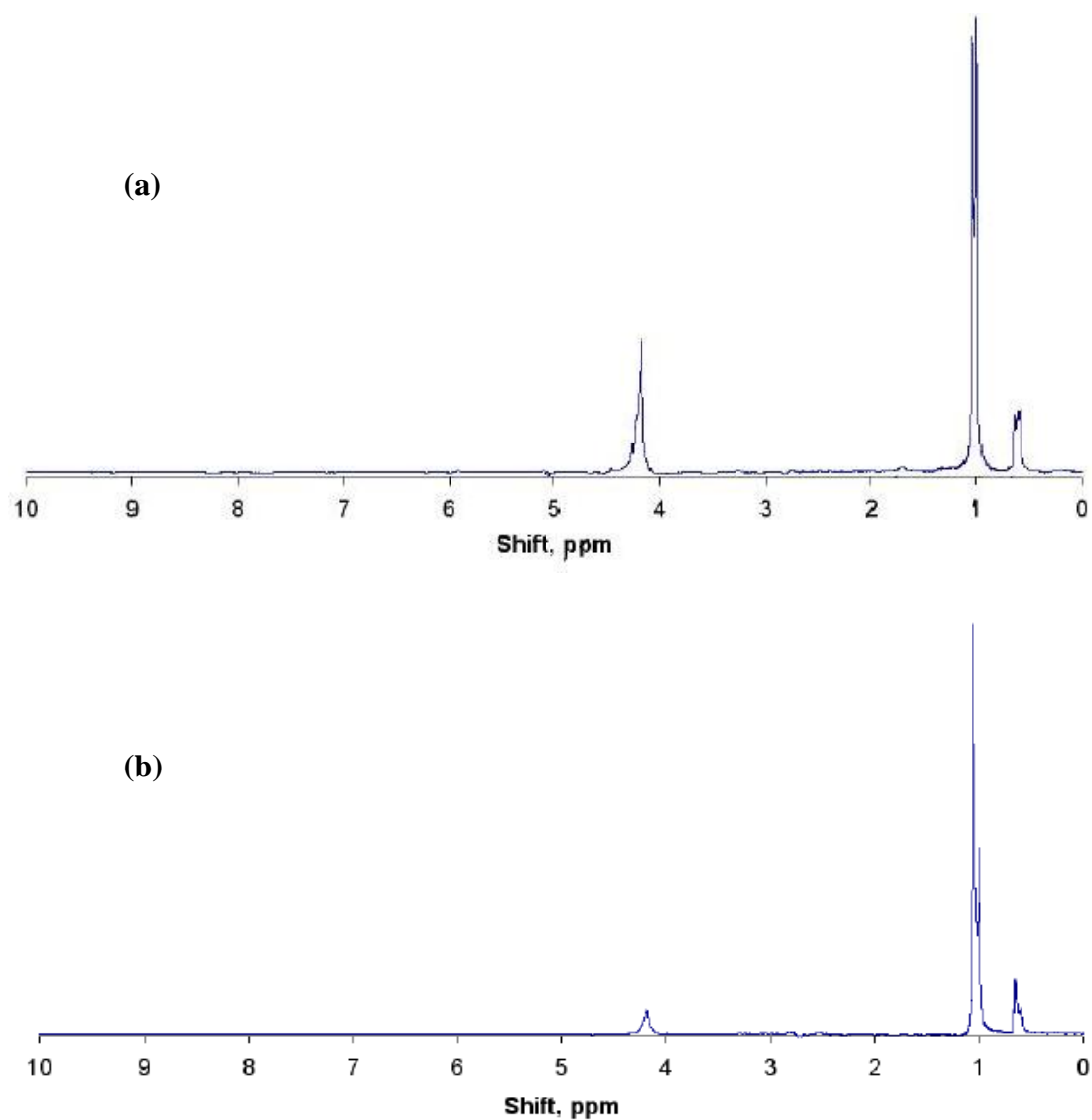


Figure 8. ^1H MAS NMR spectrum obtained at 14.1T with spinning at 30 kHz of (a) ReCo-wax and (b) CeCo-wax.

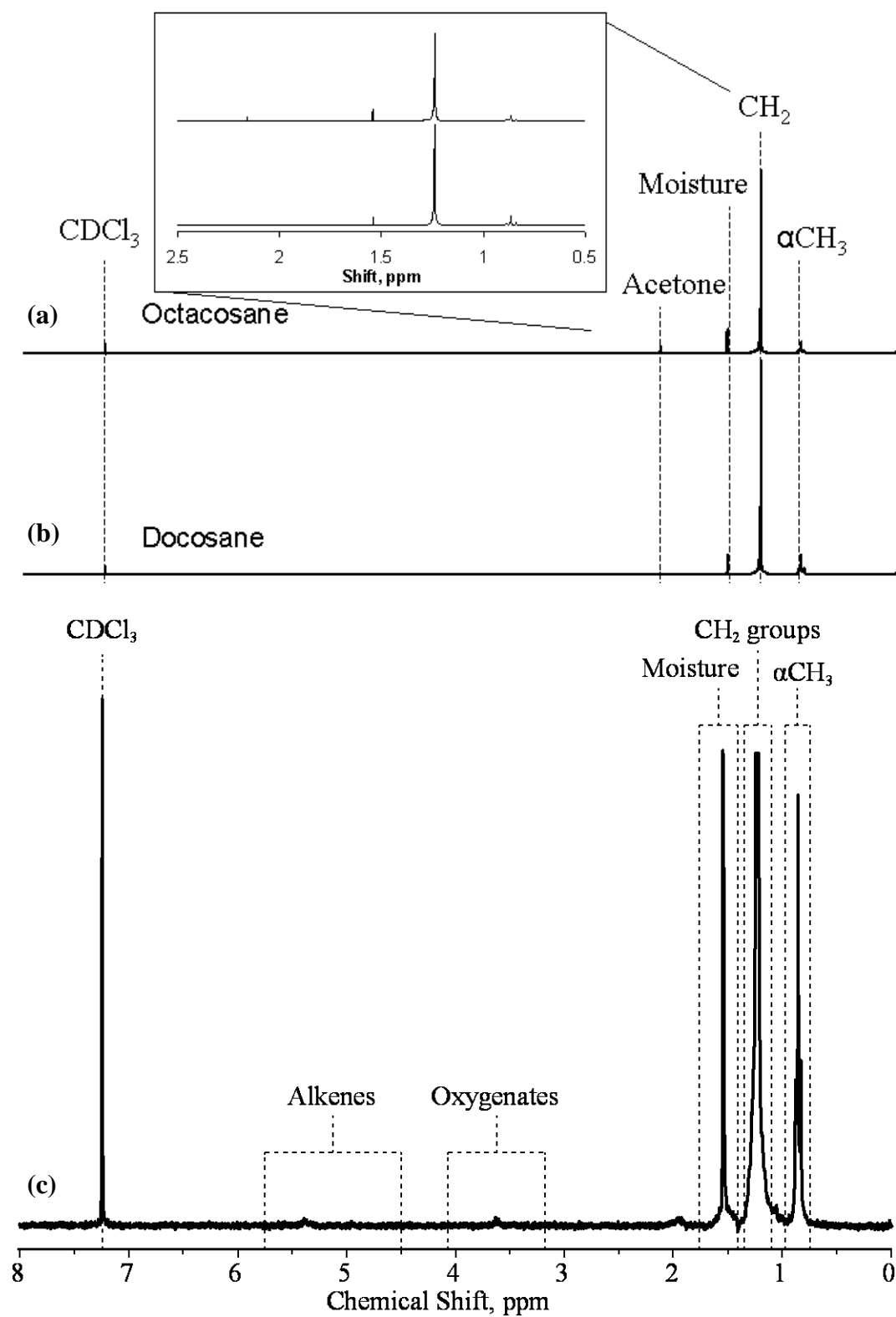


Figure 9. ^1H solution-state NMR spectra taken at a field of 6.35 T of (a) octacosane ($\text{C}_{28}\text{H}_{58}$), (b) docosane ($\text{C}_{22}\text{H}_{46}$) and the Co-wax.

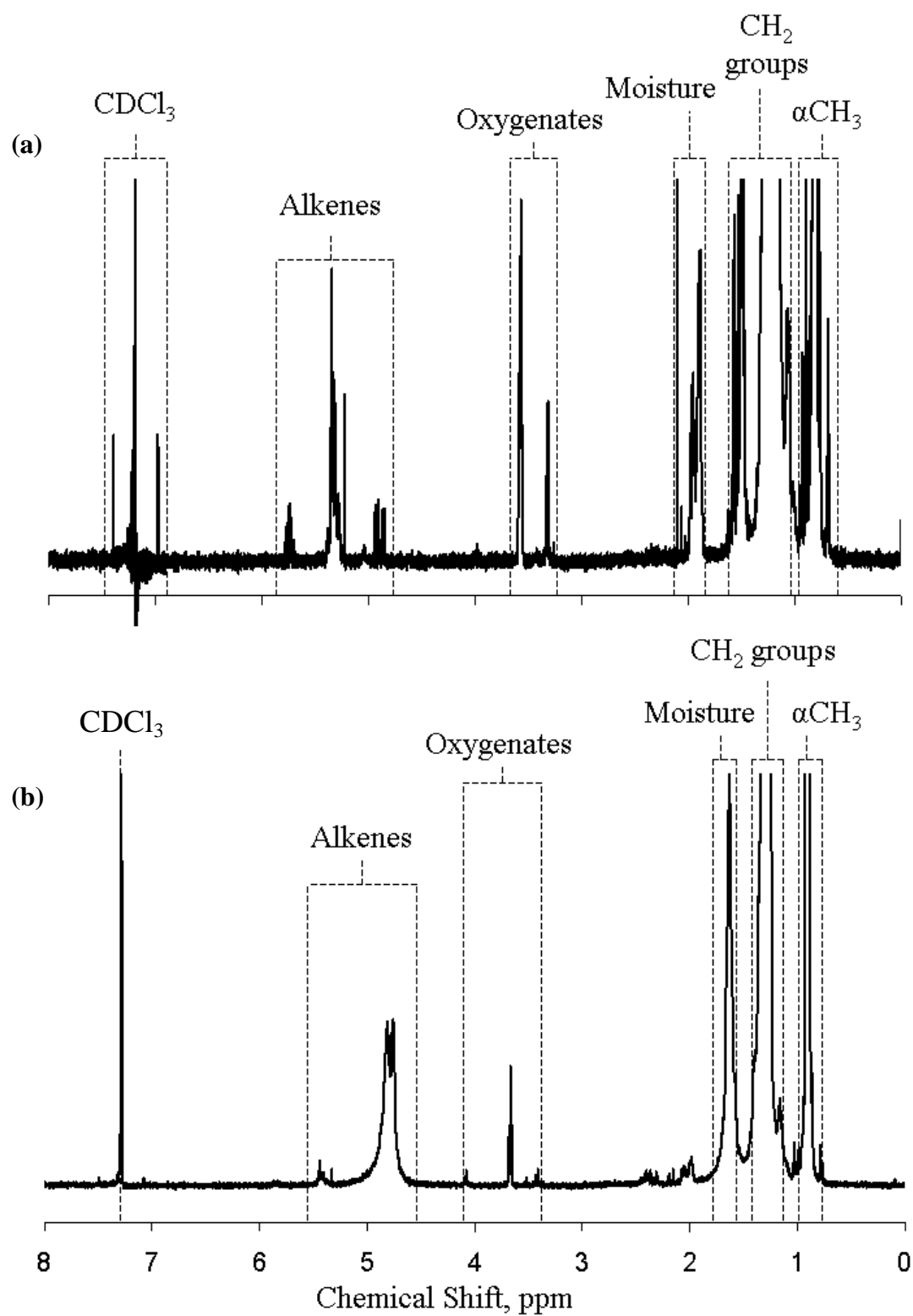


Figure 10. Solution-state ^1H NMR spectra taken at a field of 11.75 T of (a) ReCo-wax and (b) CeCo-wax.

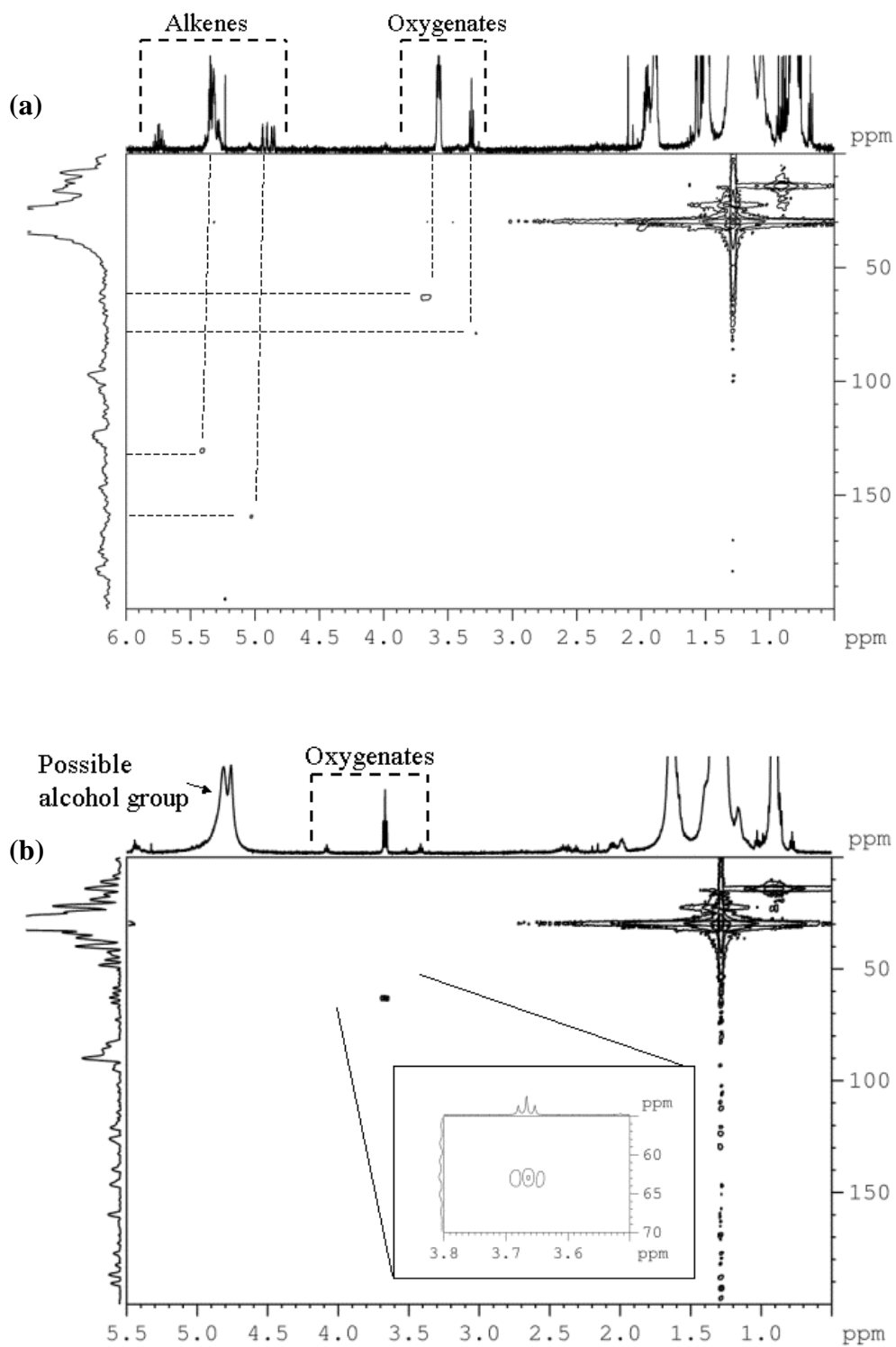


Figure 11. 2D HMQC correlation NMR spectra taken at a field of 11.75 T of (a) ReCo-wax and (b) CeCo-wax. The x -axis displays the ^1H spectra and the y -axis displays the ^{13}C spectra.

Tables

Table 1. Summary of results of the calculated values for N_C for a range of hydrocarbon waxes calculated using solution-state ^1H NMR.

| Sample | N_C calculated using solution-state NMR (± 0.5) |
|---|---|
| Docosane ($\text{C}_{22}\text{H}_{46}$) | 22.4 |
| Octacosane ($\text{C}_{28}\text{H}_{58}$) | 28.4 |
| Co-wax | 20.0 |
| ReCo-wax | 21.4 |
| CeCo-wax | 21.0 |

Table 2. Summary of the calculated concentrations of olefins and oxygenates in the waxes. The values were calculated using solution state ^1H NMR.

| Sample | Olefins / mol% | Oxygenates / mol% |
|---|----------------|-------------------|
| Docosane ($\text{C}_{22}\text{H}_{46}$) | - | - |
| Octacosane ($\text{C}_{28}\text{H}_{58}$) | - | - |
| Co- wax | 0.43 | 1.63 |
| ReCowax | 0.46 | 0.35 |
| CeCo-wax | 3.32 | 0.18 |